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MEASURING CIRCUIT FOR AUTOMATIC MEASUREMENT OF ELECTRON-CAPTURE DETECTOR CHARACTERISTICS

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SUMMARY

A voltage impulse generator with a varying repetition time for supplying electron-capture detectors is described. The generator allows the measurement of the detector ionization current with a change of the pulse repetition time (t_r) from 1 to 5200 μsec in 8.3 min. The generator allows the measurement of the detector characteristics for an impulse duration time in the range 0.25–90 μsec. A gas sample injector that enables a constant mass of a sample component to be inserted cyclically into the carrier gas stream so as to trace the detector signal as the repetition time of the impulses supplying the detector changes is described. The influence of the electrode geometry, carrier gas purity and detector temperature on the value of the ionization current and the detector signal is discussed.

INTRODUCTION

Electron-capture detection (ECD) has a high selectivity towards halogen compounds and gives low detection limits and is widely applied in many analytical problems. However, the physical basis of its operation and the mathematical relationships between the signal and the concentration of a sample substance are still developing. The variety of physical processes during the detector operation and especially their variability with time make some assumptions necessary. These give a rough description of the detector operation in advance, but consistent with the experimental results within the accepted assumptions.

Verification of theoretical detector models with experimental data requires a knowledge of the relationships between the detector ionization current and its signal, and the external parameters such as the means of supply and of the measurement of the detector signal and also internal factors such as the activity of the radioactive source, electrode geometry and the nature and purity of the carrier gas.

The impulse generator and the measuring circuit presented here permit the rapid measurement of ECD characteristics. This circuit may be applied for investigative, purposes during the testing of the influence of the electrode geometry and the composition of the carrier gas, especially during the operation of the detector with oxygen or nitrous oxide doping, and for practical purposes when establishing the optimal repetition time of the supply pulses in order to optimize the conditions of the detector operation.

IMPULSE GENERATOR AND MEASURING CIRCUIT

Fig. 1 illustrates the operating principles of the impulse generator with the frequency changing automatically. The circuit includes two series of binary counters and a digital comparator with logical states of both series. The first rapid series counts rectangular pulses of 100 kHz frequency obtained from a quartz generator. The second slow series of binary counters counts impulses of period 1 sec obtained from an auxiliary multivibrätor. The counting process carried out by the first series is interrupted every time the states of the counters in both series become equal. The signal from the comparator sets the first series to zero and puts in motion the output stage of the generator, which generates the standard impulse supplied to the detector. The changes of frequencies of the impulses that supply the detector occur simultaneously with the changes of the state of the slow series of counters.

In the circuit presented, during every 1 sec of the sampling stage the repetition period of the impulses supplying detector changes by 20 μsec. The accepted change of the repetition period is a compromise between the time of measurement of the detector characteristics, the accuracy of measurement and the time necessary for equilibrium of the electron-capture processes in the detector to be achieved.

In the generator described, a change of the impulse repetition from 1 to 5200 μsec proceeds in 8.3 min. The generator also makes possible a change in the voltage duration period within the range 0.25–90 μsec with an accuracy $\pm$ 0.1 μsec. The amplitude of the voltage impulse is 60 V. Fig. 2 shows the electronic circuit of the impulse generator. Fig. 3 shows possible systems for supplying the detector with the impulse voltage and for measurement of the ionization current. Fig. 3a refers to the detector with two insulated electrodes. The voltage source U_k makes possible the

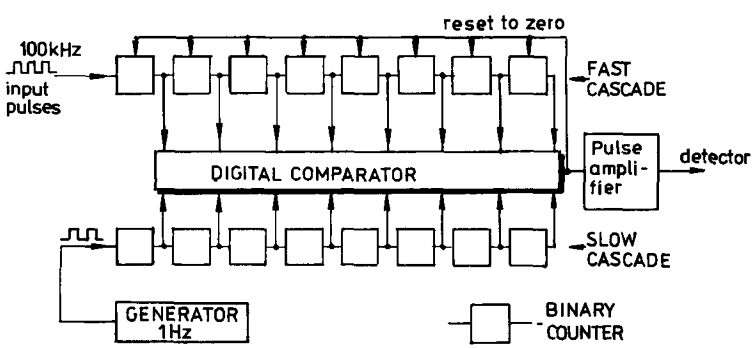

Fig. 1. Schematic diagram illustrating the principle of operation of the impulse generator with changing time of impulse repetition.

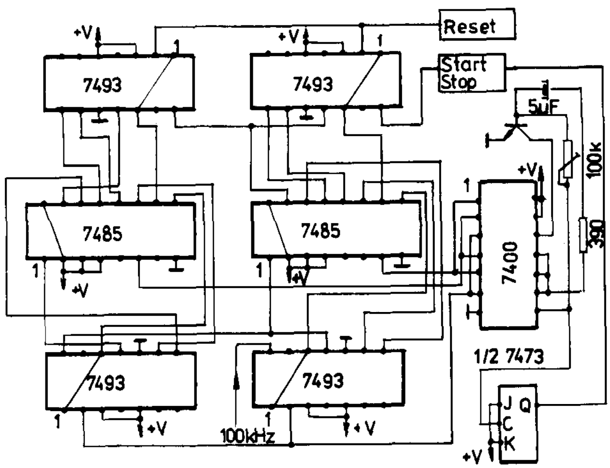

Fig. 2. Electronic arrangement of the generator.

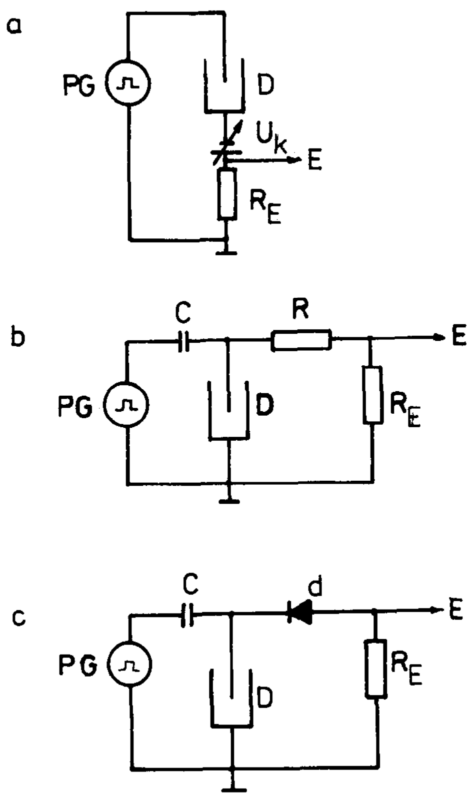

Fig. 3. Schemes of feeding and the ECD ionization current measurement. D = Detector; PG = voltage impulse generator; E = output to the electrometer; R_E = electrometer resistance; C = coupling capacitance; R = separating resistance; d = diode; U_K = voltage compensation source; a = circuit for the detector with two insulated electrodes; b, c = circuit for the detector with an earthed cathode.

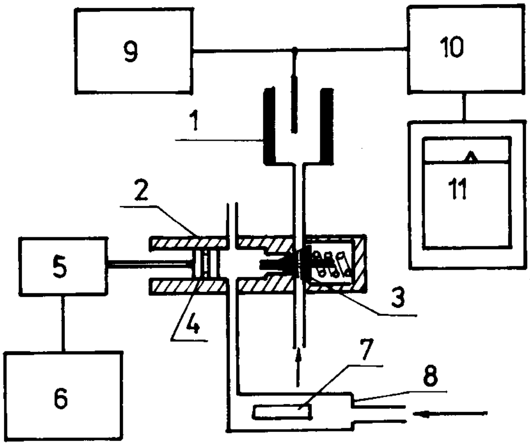

Fig. 4. Scheme of the circuit for measurement of ECD characteristics. 1 = Detector; 2 = gas sample injector; 3 = valve; 4 = piston; 5 = electromagnets; 6 = time relay; 7 diffusion standard; 8 = thermostat; 9 = voltage impulse generator; 10 = electrometer; 11 = recorder.

compensation of the detector contact potential. In the circuit shown in Fig. 3a, voltage impulses are applied directly to the collecting electrode of the detector. Fig. 3b and c refer to the detector in which the electrode including the radioactive source is earthed. In these circuits voltage impulses are led to the collecting electrode by the capacitance C. The electrometer E is connected to the collecting electrode by the resistor R as in Fig. 3b or by a separation diode as in Fig. 3c. The resistor R_E in Fig. 3 is the measuring resistance of the electrometer.

Fig. 4 illustrates the circuit for the measurement of the detector characteristics. The detector (1) is supplied with carrier gas flowing through the injector (2) via a valve (3). The piston (4) in the injector (2) is moved by an electromagnetic valve (5), guided by a time relay (6). The carrier gas bearing molecules of the sample substance,

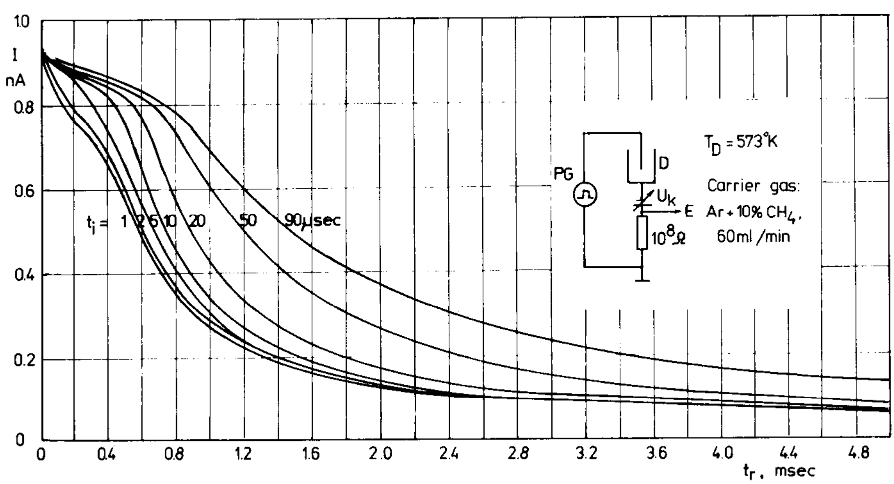

Fig. 5. Dependence of ECD ionization current on the repetition time of impulses, t_r, for various durations of the impulses, t_i, for the circuit illustrated.

e.g., from a diffusion standard (7) placed in a thermostat, flows through the injector (2). The detector is electrically supplied from the voltage impulse generator (2) with the growing repetition impulse time (9) and its ionization current, measured by means of an electrometer (10), is recorded on a recorder (11). By changing the stroke of the piston (4) in the injector (2), the amount of substance dosed into the carrier gas flowing through the detector can be changed.

EXAMPLES OF MEASUREMENTS OF ELECTRON-CAPTURE DETECTOR CHARACTERISTICS.

Figs. 5–7 give results of measurements of the ionization currents in the measuring circuits illustrated. The detector examined, which was of our own construction, had a ^{63}Ni source. The detector temperature was 573°C in each instance and as carrier gas was given argon + 10% methane at a flow-rate of 60 ml/min.. Measurements were carried out for impulse duration times from 1 to 90 μsec. On comparing the curves in Figs. 5–7 it can be seen that the system used to supply the detector and the measurement of its ionization current influence the shape of the detector current characteristics.

Fig. 8 gives the characteristics of the detector operating with the measuring circuit illustrated and with nitrogen as the carrier gas at a flow-rate of 60 ml/min. By means of the injector shown in Fig. 4 an amount of 0.6 pg of Freon F-11 was periodically inserted into the stream of carrier gas flowing through the detector. Curves 1, 2 and 3 in Fig. 8 refer to the detector operating at 323, 423 and 573°K, respectively. The zero lines for each line have been shifted in order to present the characteristics more clearly. The temperature and the time of impulse repetition at which the detector signal has its maximum value is shown on this figure.

Fig. 9 presents analogue measurements with the measuring circuit illustrated with argon + 10% methane gas at a flow-rate of 60 ml/min and a detector temperature of 573°K. Freon F-11 of mass m_1 for curve 1, 2 m_1 for curve 2, 3.2 m_1 for curve

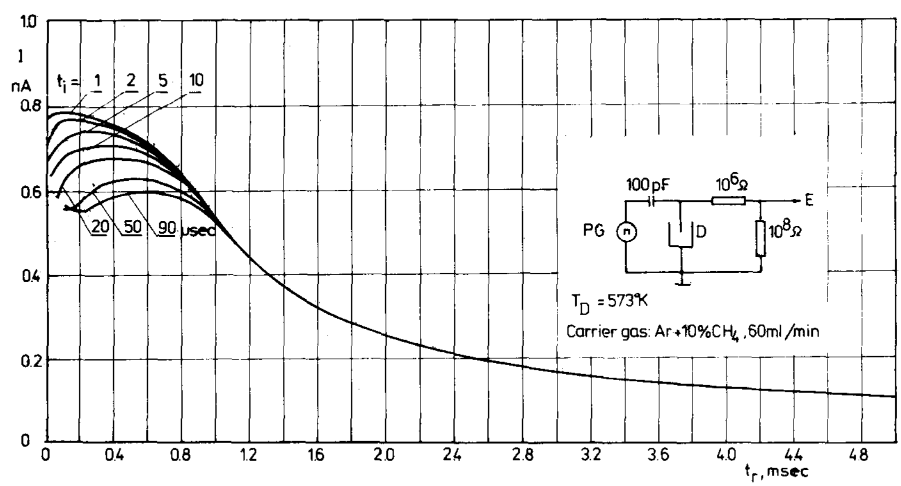

Fig. 6. As Fig. 5, for the circuit illustrated.

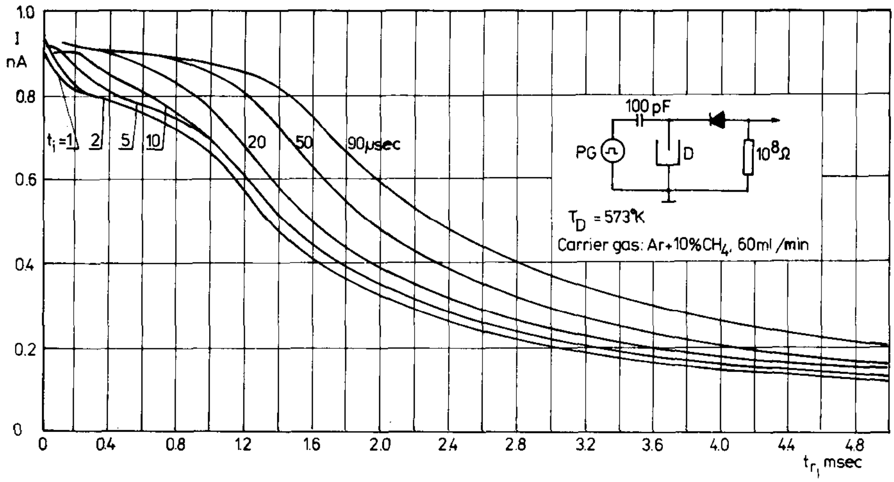

Fig. 7. As Fig. 5, for the circuit illustrated.

3 and 4.8 m_1 for curve 4 were inserted into the carrier gas stream. The zero lines for particular curves have been shifted for clarity.

The measurements presented in Fig. 9 illustrate how the optimal repetition time of supplying the impulses is reduced as the mass of sample increases. Fig. 10 shows the influence of impurities in the carrier gas on the course of the current

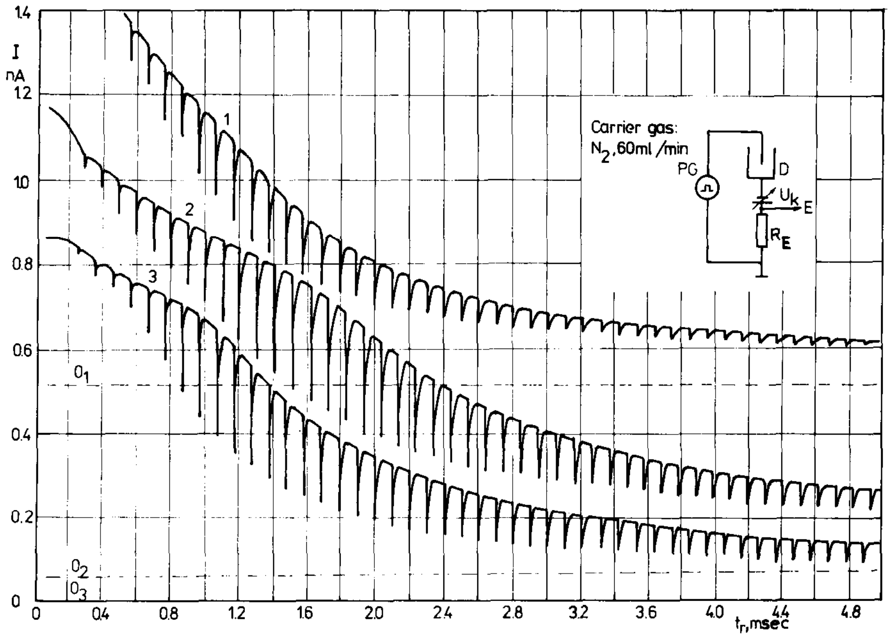

Fig. 8. Dependence of the ECD ionization current and the detector signal on the repetition time of impulses using the circuit illustrated. The impulse duration t_i = 5 μs. A 0.6-pg amount of Freon F-11 was inserted in the carrier gas stream in the circuit shown in Fig. 4. Detector temperature: 1, 323°K; 2, 423°K; 3, 573°K. 0_1, 0_2, 0_3 = zero levels for curves 1, 2 and 3, respectively.

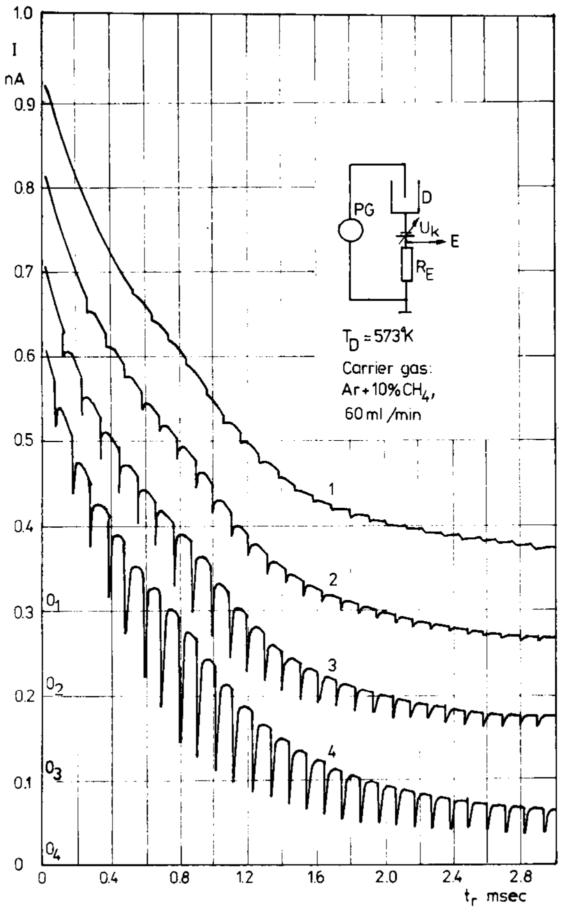

Fig. 9. Dependence of ECD ionization current and signal on the repetition time of impulses for various masses of added sample: Measurements were carried out with the circuit illustrated. 1, Sample mass m_1; 2, sample mass 2 m_1; 3, sample mass 3.2 m_1; 4, sample mass 4.8 m_1. 0_1, 0_2, 0_3, 0_4 = zero levels for curves 1, 2, 3 and 4, respectively.

characteristics of the detector and the change of the detector signal. Measurements were carried out with the circuit illustrated with nitrogen as the carrier gas at a flow-rate of 60 ml/min, containing 0.5 ppm of impurities; about 0.1 pg of Freon F-11 was periodically inserted into the gas. The detector temperature was 573°K. Curve 1 refers to the detector operating with pure carrier gas and curves 2, 3 and 4 refer to carrier gas to which about 10^{13}, 10^{15} and 10^{16} oxygen molecules per second, respectively, had been continuously added. Fig. 10 clearly illustrates the influence of carrier gas impurities on the course of the detector characteristics and the gradual fading of the detector signal.

In an electron-capture detector, the contact potential between two electrodes in an ionized gas is observed, and its value depends on the materials of construction and the activity of the radioactive source. The contact potential assumes a positive or negative polarity and influences the course of the detector current characteristics

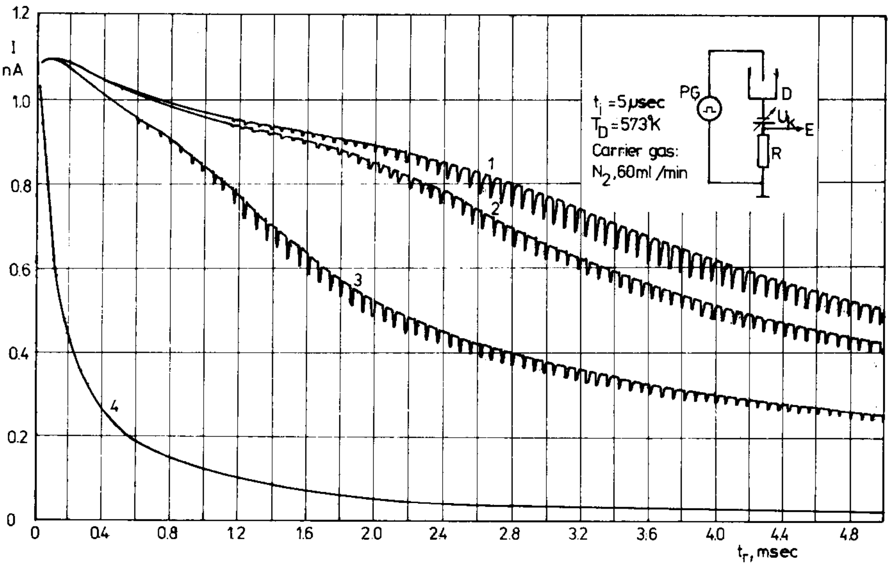

Fig. 10. Dependence of ECD ionization current and signal on the repetition time of pulses for various concentrations of carrier gas impurity using the circuit illustrated. 1, Carrier gas impurity 0.5 ppm; 2, 3 and 4, 10^{13}, 10^{15} and 10^{16} molecules/sec, respectively, of oxygen additionally inserted.

and its detectability level. The voltage source U_k in Fig. 3a allows compensation of the contact potential and the measurement of detector characteristics, for which the ionization current approaches zero, while the repetition time of the detector-supply impulses approaches infinity. If there is no possibility of compensating the contact potential in the measuring circuit, then for a repetition time approaching infinity the ionization current approaches the value of the constant current I_K caused by the contact potential. Fig. 11 shows the ECD characteristic with the indicated level of the constant current $-I_{K_2}$ with negative polarity. Curve 2 for $t_r \rightarrow \infty$ approaches the $-I_{K_2}$ of the detector current. Level 0 in Fig. 11 represents the constant current $-I_{K_2}$ compensated to zero and curve 3 approaches this zero value at infinity. The compensation voltage source U_K in Fig. 3a makes it possible to simulate the value of constant current I_K and to observe the detector characteristics for t_r approaching infinity. This sutation is illustrated by curves 1, 4, 5, 6 and 7 in Fig. 11, for which the value of the constant current I_K has been forced to the example current levels $-I_{K_1}$, I_{K_4}, I_{K_5}, I_{K_6}, I_{K_7}. The above example values of the constant current I_K illustrate the way in which the polarity and the value of the constant potential influence the shape of the ECD characteristics.

Figs. 12–15 illustrate the influence of the electrode geometry of the detector on the current characteristics. In each instance the same detector was used at a temperature of 573°K with the measuring circuit shown in Fig. 3c and the carrier gas, was nitrogen at a flow-rate of 60 ml/min. The arrangement of the electrodes is illustrated. In the electrode arrangement A in Fig. 12 the anode is placed above the level of the top of the cylindrical radioactive source. In arrangements B in Fig. 13 the anode is at the level of the radioactive source. In arrangement C in Fig. 14 the electrode is inserted half way into the radioactive source and in arrangement D in Fig. 15 the

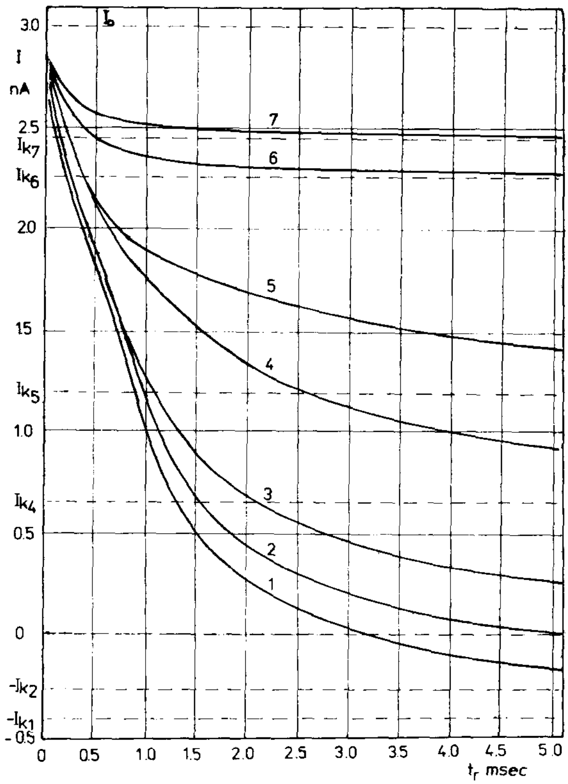

Fig. 11. Influence of the contact potential and its polarity on the course of ECD current characteristics. I_{K1}–I_{K7} = values of the constant current caused by contact potential or simulated by U_K voltage source for curves 1–7, respectively.

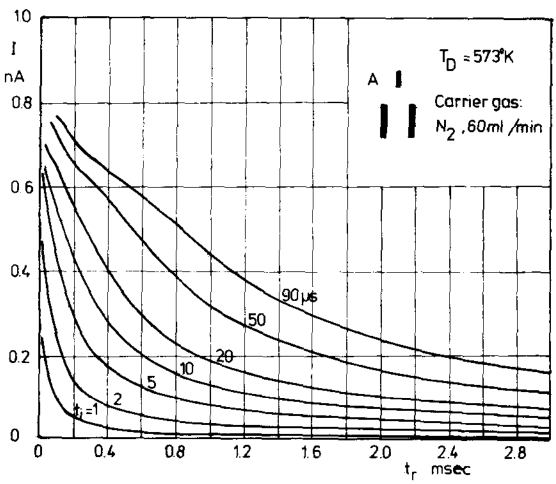

Fig. 12. Dependence of ECD ionization current on the repetition time of impulses for various periods of impulse duration for electrode arrangement A and the measurements conditions indicated. Measurements were carried out with the detector supply circuit shown in Fig. 3c.

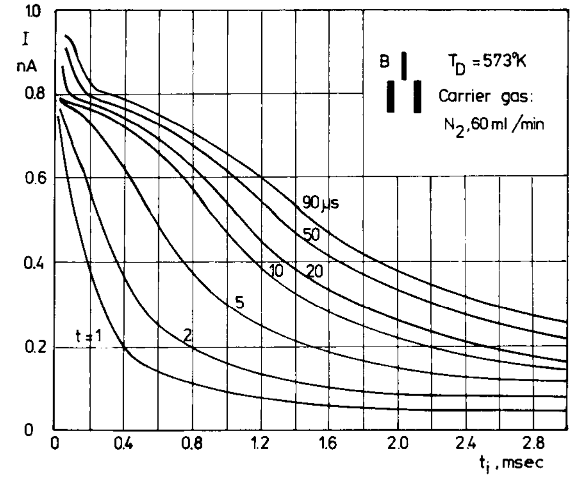

Fig. 13. As Fig. 12, electrode arrangement B.

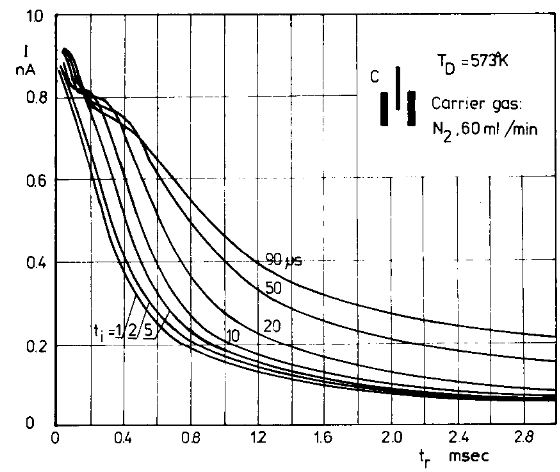

Fig. 14. As Fig. 12, electrode arrangement C.

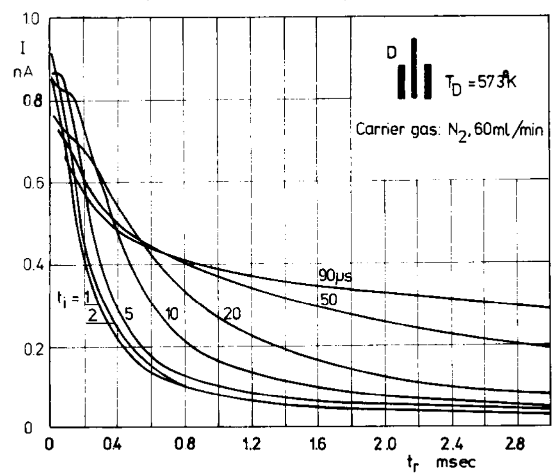

Fig. 15. As Fig. 12, electrode arrangement D.

electrode in inside the source along its length. The inner diameter of the radioactive source was 10 mm and its height was 15 mm. The diameter of the anode was 1.5 mm. The characteristics presented in Figs. 12–15 illustrate the effect of the geometrical arrangement of the electrodes on the value of the ionization current and its dependence of the detector-supply voltage impulses.

CONCLUSIONS

The ECD characteristics presented in Figs. 5–15 show testing possibilities for the impulse generator on changing the impulse repetition time and the measuring circuit illustrated in Fig. 4. The characteristics presented illustrate the way in which the detector ionization current depends on the electrode geometry, the duration of the impulse t_i and impurities in the carrier gas. In models proposed for electron-capture detectors, *e.g.*, those of Lovelock[1], Wentworth and Chen[2] and Connor[3], the influence of the electrode geometry on the detector ionization current was not taken into account. Gobby *et al.*'s model[4] and the previous ones do not take into account the influence of the duration of the voltage impulse on the detector ionization current. Descriptions of detector operation in the literature do not include the measuring circuit, which, as can be seen in Figs. 5–7, has an important effect on the measured ionization currents. The complex shapes of the curves in Figs. 12–15 for the arrangements of the electrodes A, B, C and D, especially for short repetition times of the supply pulses for a wide range of impulse duration t_i, give much information on gathering electrons and positive ions in the detector and the formation of a positive space charge between the detector electrodes, and will be useful in further development of Gobby *et al.*'s "space charge" model[4].

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